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The determination of the distribution coefficient of radium and of its isotope ThX between fused and crystalline calcium nitrate

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The anhydrous nitrates of calcium, strontium, barium and lead, crystallising in the form of rectilineal octahedrons, form, as is well known, an isomorphous group.

In the case of crystallisation of the solid phase from the aqueous solution the distribution coefficient of radium was determined for three members of this group only: for nitrates of barium (Bibl. 1), strontium (Bibl. 2) and lead (Bibl. 3). In all three cases the distribution coefficient D was found to be of a magnitude [illegible] which is evidence of the fact that the enrichment by the micro-component occurred in the solid phase, since the distribution coefficient D shows how much richer the crystals are as a micro-component than the salt remaining in the solution $D = \frac{x(100-y)}{y(100-x)}$ in which x and 100 - x are the quantity of the radioclement in percent converted into crystals and remaining in the solution (or melts), and y and 100 - y the quantity of the isomorphous salt in percent, converted into crystals and remaining in the solution (melt). The distribution coefficient was not determined for calcium nitrate since this crystallizes from aqueous solutions in the form of tetrahydrate, giving monoclinic crystals, which are non-isomorphous with the crystals of anhydrous radium nitrate. The potassium nitrate crystallizes from the melt in the form of an anhydrous salt which is isomorphous with radium nitrate and therefore in this case the distribution coefficient of radium can be determined for this fourth member of the isomorphous group.

The distribution coefficients of radium between the melt and the crystals of the three other isomorphous salts were determined by the authors in a preceding report (Bibl. 4).

Experimental part.

In this investigation the authors used the method developed earlier (Bibl. 4). The distribution coefficient of radium between the melt and the crystals of calcium nitrate were studied in the system $Ca(NO_3)_2$ - $Ra(NO_3)_2$ - $Na(NO_3)_2$.

Anhydrous calcium nitrate was obtained by careful drying of the tetrahydrate at 150°. The sodium nitrate was also dried at the same temperature. Radium and its isotope ThX were used as a determining component, the latter being obtained by the method of collecting emission atoms on a negatively charged plate. The measurement of the activity of the specimens of the melt before and after separation of the solid phase for determining the percentage of radium converted into the solid phase, was effected by the emission method.

Before experiments were performed on the distribution, a curve was plotted of the fusibility of th[illegible] $Ca(NO_3)_2$ - $NaNO_3$. The curve was plotted up to 70 mol % of calcium nitrate, since a mixture with a greater content of calcium nitrate begins to opalesce and the calculations become inaccurate.

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According to the authors' data the melting point of the eutectic of this system is equal to 230°, and the content is equal to 49.5 mol. % of calcium nitrate. Menezies and Britt (Bibl. 5) give a melting point of the eutectic equal to 236°, and a content equal to 50 mol % of calcium nitrate. The amount of the solid phase separated [$Ca(NO_3)_2$] was calculated according to the curve of fusibility of the system and the content of the initial and final melts. The results of the tests for determining the distribution coefficient of radium between the melt and the crystals of calcium nitrate are given in Table I.

ThX was taken in tests 4 and 9 as a micro-component, and radium in the remaining ones. The tests were effected without mixing, since it was demonstrated (Bibl. 6) that the speed of the equilibrium determination during separation of the solid phase from the melt is identical both during mixing of the melt and in the absence of mixing. Tests 9 and 10 were effected by the method of recrystallisation of the excess calcium nitrate in a melt of a definite content at a specific temperature for 4 hours, which enables the quantity of the solid phase separated into a precipitate to be increased without an increase of temperature. All the remaining tests were performed according to the method of separating the solid phase from a saturated melt.

It will be seen from fig. 1 that the distribution coefficient remains a constant value, on an average equal to unity, whatever the quantity of the solid phase separated. The quantity of the solid phase changed from 30 to 74.3%. From these data and those obtained earlier on the investigation of the distribution coefficients of radium between the melt and the crystals of the isomorphous salts we are in a position to set up the following summarized table (Table 2) for all four members of this isomorphous group.

It will be seen from Table 2 that in the case of the distribution of radium between the melt and the crystals of barium and strontium nitrates the distribution coefficient D is equal to 0.4, i.e., in this case an enrichment of the melt by the micro-component occurs. With the distribution of radium between the melt and the crystals of calcium and lead nitrate, D is equal to unity, which is evidence of the equilibrium distribution of the micro-component between the melt and the crystals of these salts. Thus, during distribution of the radium between the melt and the crystals of the isomorphous salts two interesting peculiarities are observed.

The first peculiarity lies in the fact that the mixed crystals are more easily formed by radium not with its nearest group neighbours, i.e., barium and strontium, but with more distant elements, calcium and lead, i.e., in this isomorphous group the tendency in the case of analogous elements to form mixed crystals with radium is not consistent with the difference of their radii. as will be seen from Table 3.

The second peculiarity is the fact that in the systems hitherto examined by the authors relating to the distribution of radium between the melt and the crystals of isomorphous salts, no enrichment of the solid phase by the radium was observed.

Conclusions

1. The distribution coefficient of radium and of its isotope ThX between the melt and the crystals of calcium nitrate was determined.

2. It was found that also in this system in distribution of the radium between the melt and the crystals of the isomorphous salt no enrichment of the solid phase by the radium occurs.

3. It was demonstrated that radium in the isomorphous group of nitrates of Ca, Sr, Ba and Pb easily forms mixed crystals with the nitrates of calcium and lead, but not with the nitrates of strontium and barium, i.e., its nearest group neighbours.

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Tables

TABLE 1. Radium distribution between the melt and the crystals of $Ca(NO_3)_2$.

No. of test	Amount of crystallising out $Ca(NO_3)_2$ in %	Amount of Ra, converted into the solid phase in %	D
1	30.0	27.0	0.9
2	40.0	36.5	0.9
3	40.0	35.4	0.8
4	45.0	45.4	1.0
5	52.3	56.2	1.1
6	52.3	56.7	1.2
7	52.3	53.4	1.0
8	52.3	55.4	1.2
9	64.0	63.7	1.0
10	74.3	74.9	1.0
		Average	1.0

TABLE 2

The value of the radium distribution coefficients between the melt and the crystals of the nitrates of divalent metals.

Isomorphous salt	D
$Ba(NO_3)_2$	0.4
$Sr(NO_3)_2$	0.4
$Ca(NO_3)_2$	1.0
$Pb(NO_3)_2$	1.0

TABLE 3.

Radii of the ions of divalent metals

Element	Radius of ion R in A	$R_{Ra} - R_3$	Difference of radii in % (in relationship to the lesser)
Ra	1.52	-	-
Ba	1.43	0.09	6
Sr	1.27	0.25	20
Ca	1.06	0.46	43
Pb	1.32	0.20	15